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Critical Literature Review
(ANTA602)

Accurate Measurement of the Reforming of the Ozone Layer above Antarctica

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Abstract
The Montreal Protocol was accepted almost universally and successfully gained global cooperation to reduce the production and release of Ozone Depleting Substances (ODS). When Chlorofluorocarbons (CFCs) are released the free chlorine molecules that become available in the atmosphere are able to deplete the O_3 ozone molecule in a catalytic reaction allowing Ultraviolet (UV-B) radiation to enter the atmosphere. This deletion of the ozone layer was quickly acknowledged to be detrimental to human health and measures were taken. There is some concern that there are ODSs still being released from some sources and that there are residual ODSs in equipment yet to deteriorate.

This review examines the present measurements of the ozone levels in the Antarctic stratosphere, how the increased use of modelling has improved the accuracy of the measurements and led to a clearer understanding of the dynamic mechanisms that reform the ozone hole each year. The polar vortex formation and the dynamically induced changes in the troposphere are the main drivers in the appearance of the ozone hole each year above the Antarctic. Mt Erebus has recently been found to be a significant source of ozone destroying gases. As these dynamic systems are more clearly understood and accounted for the variable annular ozone levels are able to be accurately assessed for the possible future recovery of the ozone hole to pre-1980 levels.

1. **Introduction**

The annular spring formation of the ozone hole above Antarctica has been widely studied during the last forty years since it was first discovered that the stratospheric ozone layer was in danger of becoming depleted. Molina and Rowland recognized the potential for chlorofluorocarbons (CFCs) and other ozone depleting substances (ODSs) to deplete the stratospheric ozone in 1974 (1). This early warning was heeded by scientists and governments around the world who used the 1987 Montreal Protocol to put in place regulations that led to a gradual but effective reduction and phasing-out the global production and consumption of ODSs. As a consequence there were less CFCs emitted into the atmosphere. The abundance of ozone-depleting substances, now measured by Equivalent Effective Stratospheric Chlorine (EESC) was found to be at a high level at the beginning of the 20th century and has subsequently declined (World Meteorological Organization (WMO), 2006) (2).

The ozone layer protects life on our planet by shielding it from harmful Ultraviolet B (UV-B) radiation. Exposure to even small increases in UV-B radiation can have serious impacts on human health. The productivity of marine phytoplankton is also reduced, as the photosynthesis process of these organisms is lowered markedly, therefore affecting the wider ocean food web. Recent studies have concluded that ozone depletion can be a driver to influence climate, which in turn can have significant implications for the Southern Hemisphere's ecosystems (3) and that this ozone depletion could also be a cause of the increased formation of Antarctic Sea ice (4). The accurate assessment of the degradation and reforming of the annular ozone hole over the Antarctic is therefore seen to be important, as signs are looked for that indicate the ozone hole may be returning to pre-1980 levels. There are a number of variables in the Antarctic climate which make it challenging to see any obvious trend towards the recovery of the ozone hole from annual readings. The elimination of these variables and the continual refining of the models used in predicting possible ozone levels are important steps towards understanding the actual levels of ozone now, and in the future. This review examines the improved accuracy of ozone readings, as variables are considered and eliminated, and the improved modelling techniques that can be based on the data produced since Molina and Rowland's work. Improving the accuracy of measurements and modelling and whether or not these indicate a recovery of the ozone hole to pre-1980 levels is also discussed.

2. **The mechanism of ozone depletion**

Before the work of Molina and Rowland in the 1970's it was not thought that human activity could affect the ozone layer. They were the first to theorize that a series of artificially produced volatile compounds, chlorofluorocarbons (CFCs) and other ozone depleting substances (ODSs) could destroy ozone in the stratosphere. These compounds were used in various refrigeration appliances, as the driving gas in aerosol-bottles and in the production of plastic foam and it is their very stability under normal conditions which made them seem to be so useful initially. CFCs are stable in the troposphere and can therefore be mixed up in a very slow process upwards into the stratosphere. Here they are decomposed to give free chlorine, (Cl) which is able to destroy the O_3 molecule and then reform, so that each Cl molecule can decompose several thousand ozone molecules (5). Chlorine can destroy ozone catalytically in the Earth's atmosphere through the following reactions:

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$

During the period from 1965 to about 1980 the total chlorine content in the atmosphere is estimated to have increased from about 1.2 to 2.5 p.p.b.v (parts per $10^9$by volume). This increase produced a 3-5% change in the calculated ozone in the Antarctic spring near 30km, while the calculated changes at 20km and below were less than 1%. Balloonsonde data taken during the 1980's found that the cause of the ozone loss was chemical and that the process had the following constraints: 1. It is essentially confined to the Southern Hemisphere, 2. It must be a strong function of latitude and season, 3. It must produce an acceleration of the ozone chemical loss rate from a timescale of the order of several years to about a month near 15-20km, and 4. It must increase with time over at least the last 10 years, (prior to the 1980 readings) (5).

Although there are few pollution sources in the Antarctic, CFCs are transported to the Antarctic stratosphere by the following process. CFCs are released on the ground in higher latitudes and then are transported from the troposphere in the tropics to the polar stratosphere by the Brewer-Dobson circulation. The lifetime of CFCs, which is thought to be around 6 years, means there is time for the CFCs to be completely mixed up in an atmosphere of very low temperatures at the Antarctic and this, coupled with a polar vortex that keeps the components together, leads to conditions that are favourable for the decomposition of ozone. (6) The formation of the Polar Stratospheric Cloud is linked to the formation of the ozone hole as the PSC supports the chemical reaction that activates chlorine (Cl). The free Cl molecules then destroy the ozone when sunlight reappears each August / September. The polar vortex forms only at temperatures colder than 195K, conditions achieved in the Antarctic stratosphere during the polar night (WMO, 1985). The stability of a cool polar vortex allows the PSC to form from condensation of molecules able to condense at this low temperature. Whatever mechanism controls the winter temperature controls the formation of the PSC and therefore the springtime depletion of ozone. (2) To this mix of conditions must be added the ozone depleting compounds released from Mt Erebus's volcanic eruptions.

3. **The continued presence and release Oxygen Depleting Substances**

When the Montreal Protocol called upon countries to regulate for the cessation of ODS use there was an almost universal global response to comply. The world's production, consumption and emissions of ODSs were reduced and it is thought likely that the ozone hole recovery would not have been possible without this cooperation between governments and industry. There are concerns that there are some "banks" of ODSs stored in equipment that has not yet been recovered and destroyed. This old equipment will slowly decay and deteriorate and the ODSs will eventually leak into the atmosphere. Also of concern are a small number of countries who have not completely halted emissions of ODSs. According to the 2015 WMO Bulletin 64 "Is the Ozone Layer on the Mend?"(9), there is an atmospheric abundance of carbon tetrachloride (CCl_4) and that this does not decline as fast as previously expected. This implies that there is an unknown source of CCl_4 somewhere. This finding shows the importance of continuing to independently monitor the atmospheric amounts of ODSs by effective measurements and modelling, even though the compliance to the Montreal Protocol is in place. Volcanic eruptions are also able to contribute ozone depleting chemicals as was observed in 1991 when Mt Pinatubo erupted in the Philippines and resulted in a significant ozone loss in the stratosphere.

In 2015 a study of the Antarctic stratosphere was undertaken to determine if the eruptions of Mt Erebus have been contributing ozone depleting Hydrogen Chloride (HCl) and sulfuric acid (H_2SO_4) molecules to the Antarctic stratosphere. Between 1972 and the early 1980s Mt Erebus had a vigorous level of volcanic activity that would have produced more ozone depleting substances than are being produced today (7).

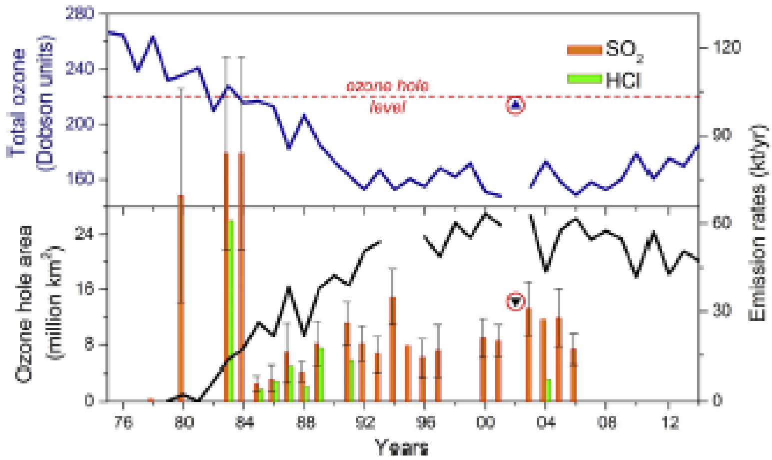

Figure 1. The September average total ozone over the Halley Bay station and the ozone hole area are shown together with emissions rates of HCl and $S0_2$ from 1976. There is an anomalously high level of ozone and ozone hole area in 2002 which is denoted by triangles. (Zuev et al , 2015)

4. **Measurement methods of ozone levels**

Several different methods are used to gain a complete and accurate measurement of the ozone hole.

Readings of ozone levels have been taken from balloonsonde, giving ozonesonde measurements, and by satellite. When both satellite and balloonsonde measurements are combined this allows for a more complete study of the Antarctic ozone hole. While satellite remote sensing provides global coverage of ozone, balloon-borne ozone sensors provide an accurate measure of the vertical profile of ozone. According to Hofmann, Johnson and Oltman in their research paper, “Twenty-two years of ozonesonde measurements at the South Pole”, this increased accuracy of reading at altitude allows accurate estimates in the total and partial column ozone when satellite measurements cannot be made due to darkness. Balloons have been used to take weekly readings for the twenty two years previous to 2009, with readings increased to two or three weekly during the rapid decline in ozone during September. (8) Hofmann, Johnson and Oltman’s 2009 paper updated earlier findings that the ozone depletion had increased during the 1986- 1995 period. Using early equivalent chlorine projections they estimated that the beginning of ozone recovery would not be seen until before the 2010-2020 period. Hofmann et al’s latest paper updates these findings. (8)

Satellite measurements have been made by TOMS (Total Ozone Mapping Spectrometer) and OMI (Ozone Monitoring Instrument) providing a continuous record of springtime ozone measurement that now spans three decades (2).

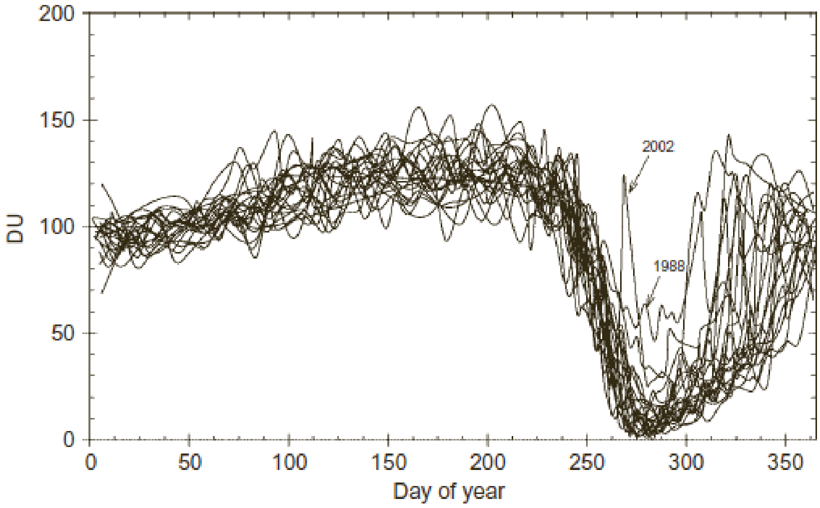

Figure 2. South Pole 14 – 21km annual column ozone from 1986 to 2007. The polar vortex was unusually disturbed in 1988 and 2002. (Hofmann et al, 2009)

5. **Measurements of the variables**

The balloonsonde readings conducted by the US National Oceanic and Atmospheric Administration at the South Pole used to calculate the ozone hole minimum in late September to early October were found to have a sizable degree of variability and reasons were suggested for this. One reason given was the presence or absence of any EESC that are present in the stratosphere in September. The winter temperature and the stability of the polar vortex are also factors. As outlined earlier the formation of the polar vortex will determine the springtime depletion of ozone, therefore linking winter temperature with ozone depletion. There is also a dynamic component to the annular ozone readings which is thought to be related to the variations of stratospheric dynamics (8).
Each of these reasons for the variability of ozone levels can also be measured, with these findings then able to be used as indicators giving the predicted level of ozone in the stratosphere.

i) The gases that cause the ozone loss can be measured. For example, CFCs and other gases can be estimated. Due to the regulatory action of the Montreal Protocol these gases previously released on the Earth's surface are declining and, as these are ozone depleting gases, the ozone hole should be recovering in response. Estimations of the Cl and Bromine (Br) inside the stratospheric polar vortex can be made by taking trace–gas measurements at the Earth's surface and then considering the atmospheric mixing that will take place (9). ODSs are not regularly measured in the Antarctic atmosphere which means that the measurements involve estimating the amount of ODSs and their behaviour over time. There are limitations to estimating standard EESC in the Antarctic. Standard measurements of EESC are inappropriate for application in the Antarctic stratosphere because age-of-air is crucial for accurate measures of Cl and Br gases. Mid-latitude fractional release rates are not able to be applied in the Antarctic stratosphere. A new algorithm was calculated to estimate EESC in various parts of the Antarctic stratosphere. The released trace gases were calculated from aircraft observations (*Schauffler* et al. 1999, 2003).The technique used was to find the fractional release rates of ODSs by combining the time series of surface observations with the correct age-of-air spectrum. Since air travels downward from the upper stratosphere into the core of the polar vortex, the estimation is that EESC trace gases spend up to 6 years in the lower Antarctic stratosphere. When using these measurements of the ODSs in conjunction with stratospheric temperature and the present size of the ozone hole each spring, the conclusion reached is that the ozone hole will recover later than first thought, with a full recovery by 2068, and that the recovery of the ozone hole will not be statistically detectable until 2024.

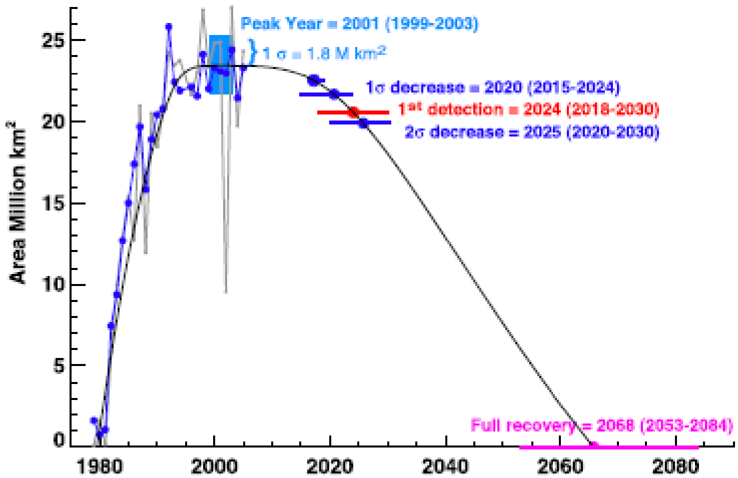

Figure 3. The ozone area averaged for September values and then extrapolated to show predicted recovery of the ozone hole. (Newman et al, 2006)

ii) Climate change in the Southern hemisphere can be linked to ozone depletion and ozone recovery. There is a quasi-biennial oscillation (QBO) in tropical winds which has links with the increased variability of the ozone levels above Antarctica since the mid-1990s. The circulation of winds drawn down from the mid latitudes have certainly influenced the conditions conducive to ozone depletion or ozone recovery and may do so increasingly in the future as the southern hemisphere experiences warmer temperatures. The temperatures of the polar vortex are able to be correlated with ozone depletion. Colder temperatures in the PSC are created when there is a weakened wave forcing of down welling of wind. The cold temperatures generated by this less dynamic force will favour Cl activation, allowing increased ozone depletion. In the years when there has been weakened wave forcing of down welling of wind, the winter time depression of temperature has continued throughout September. The warming of the rest of the planet that has led to this weaker down welling has resulted in colder temperatures observed in the polar vortex and increased depletion of ozone. In years of more intense winds the cold conditions of the vortex do not continue past August. The conditions produced by these more intense winds allow the ozone layer to recover (2). This increased cooling of the Antarctic continent has led to a higher production of sea ice which links ocean characteristics to the cold polar vortex produced by the warm westerlies. These winds have produced higher temperatures in the Antarctic Peninsula which have warmed, and will eventually melt the West Antarctic Ice Sheet (4).

6. **Predictive modelling**

Effective modelling used to predict future ozone levels needs to take into account the known levels of ozone, the amount of ODSs released into the troposphere, via human activity or by volcanic eruption, and the dynamic climate variables of the Antarctic stratosphere. Modelling experiments have also shown that the ozone hole recovery is itself an influence on the Antarctic climate. It is possible to estimate the impact of ozone recovery on the Southern Hemisphere climate by using a coupled chemistry climate model (CCM). The CCM includes global dynamics and radiation, with interactive stratospheric ozone chemistry. (3) The changes of the Southern Polar climate during recent decades have led to strengthened austral summer circumpolar westerlies which have in turn led to a cooling over the Antarctic and warming over the Antarctic Peninsula. Further changes to the Antarctic climate are expected if there are increased greenhouse gas (GHG) emissions; carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4). It is important to combine the effect these GHGs are having with the stratospheric ozone recovery and this can be looked at using CCM. These changes can be more readily understood, and future changes can be more accurately predicted, using modelling that includes coupling between ocean, atmosphere and chemistry.

7. **Limitations of present modelling**

Through the decades of ozone hole measuring and monitoring there has been a tendency towards more accurate measurement through coupled modelling together with an awareness that the ozone levels are affected by, and are also themselves a driver, of Southern Hemisphere climate. The modelling to predict future ozone levels in the Antarctic stratosphere is limited by the ability of the modelling to fit the complex and dynamic influences on the ozone level. According to *Thompson et al* (2011) these limitations are seen to be the following. Firstly, a lack of a quantitative and prognostic theory for dynamical coupling between the stratospheric and tropospheric conditions. Secondly, climate models have known deficiencies in simulating the mean climate over the high latitudes of the Southern Hemisphere and thirdly, the existing model evidence is based on relatively few clean experiments. This lack of experiments is seen as a problem due to the increase in climate model formulation and the variability of the extratropical circulation. (11) The recent conclusions drawn by *VV Zuevet al* give Mt Erebus as a constant and permanent source of HCl and SO_2 gases that are drawn up into the Antarctic stratosphere by high-latitude cyclones. Regular studies of these emissions and monitoring of these gases could be included in the modelling of the dynamic system that is the Antarctic climate therefore leading to more accurate measures of ozone and the gases that destroy it.

8. **Conclusion**

Following Molina and Rowland's discovery for the potential hazards of ODSs, the Montreal Protocol was a successful agreement leading to a reduction in the production, use and emission of these substances. Ozone loss in the atmosphere has a detrimental effect on the human health as the increase in UV-B radiation can lead to increased incidence of some cancers and a reducing of the photosynthesis production of marine plankton thereby affecting ocean food webs.
Further independent monitoring is needed to further reduce the release of ODSs into the atmosphere, as even small amounts of these substances can have an impact on the level of ozone in the atmosphere. There is some concern that "banks" of ODSs in old equipment have yet to be released as they eventually deteriorate.

To measure the levels of ozone in the atmosphere both balloonsonde, which measures the vertical profile of ozone in the atmosphere, and satellite readings, that are able to give a global picture of ozone levels, can be combined to give a more accurate measure of the ozone levels.
The time of most interest when taking ozone measurements is the period from August to September. It is at this time each year when the results of ozone depletion by ODSs in the atmosphere can be observed, leading to the formation of the ozone hole above the Antarctic. Yearly observations have shown fluctuations in the size of the ozone hole. Over recent studies there is growing awareness that the ozone hole does not form merely in response to the presence or absence of ODSs, but that there are other influences that will determine the level of ozone over the Antarctic each spring.

When measuring the amount of ozone in the atmosphere and predicting the recovery of the ozone hole the other variables that need to be considered are firstly, the Antarctic winter temperatures that lead to the formation of the polar vortex each year. These cool temperatures are a driver for the springtime depletion of ozone. The colder the polar vortex temperatures the higher the level of ozone depletion.

The dynamic system of climate that forms the polar vortex then needs to be taken into account. The release of GHGs into the troposphere has begun to change the wind patterns throughout the globe and these in turn are influencing the formation of the polar vortex. In particular climate change in the Southern hemisphere has formed increased warmer westerly winds in the troposphere which lead to cooler Antarctic stratosphere temperatures.

As more sophisticated modelling techniques have been developed the raw data from ozone measurements has been combined to give a greater understanding of the dynamic system leading to more accurate interpretation. The observed changes can be more readily understood, and future changes can be more accurately predicted, using modelling that includes coupling between ocean, atmosphere and chemistry.

The reduction of the ODSs that destroy ozone being released into the atmosphere and the dynamically induced changes that cool the Antarctic stratosphere and therefore lead to increased ozone depletion are the two main influences determining the size of the ozone hole. On balance, not with-standing years of magnitude like those in 1987, 1988 and 2002, which may again occur in the future and may be linked to dynamically induced changes, the ozone hole appears to be stable and pre-1980 levels are thought to be possible in the later part of this century. (2) The size of the ozone hole is able to more accurately be measured as other influences have been able to be isolated by using CCCM modelling techniques. Further study that observes correlations between Mt Erebus eruptions, Antarctic stratospheric ozone levels, the increases in global CO_2 emissions, the changing tropospheric circulation in the Southern Hemisphere and the increasing sea ice cover in the Antarctic.

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